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CR 56449
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GLOBE-UNION INC.
MILWAUKEE 1, WIS.



ELECTRONICS DIVISION



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Contract NAS3-2790

3RD QUARTERLY REPORT

Reporting Period: February 1, 1964
to April 30, 1964

THE DEVELOPMENT OF HIGH ENERGY
DENSITY PRIMARY BATTERIES,
200 WATT HOURS PER POUND OF
TOTAL BATTERY WEIGHT MINIMUM

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INTRODUCTION

The objective of this research program is to develop a primary battery with an energy density of at least 200 watt-hours per pound of total battery weight.

We have now placed significant emphasis on the development of an aprotic electrolyte of high conductivity which is essential in obtaining good battery performance. In this respect our experimental investigation has been primarily directed toward a clarification of the basic factors influencing the behavior of nonaqueous electrolytes.

The electrochemical tests have also been made to study the behavior of the electrodes in the electrolytes possessing favorable electrolytic conductances.

I. OVERALL PROGRESS

A. Electrolytic Conductivities of Electrolytes

1. Qualitative Screening. In order to permit rapid screening, the solute and the solvent were mixed in such a proportion so that a one molal solution resulted whenever complete solution of the solute occurred. In most cases complete solution did not occur. Thus in most cases the conductivity values obtained represent those of saturated solutions. Where both complete solution and favorable conductance are observed, the systems are then investigated quantitatively.

In addition to dimethyl formamide (DMF) and propylene carbonate (PC), we selected tetramethyl urea (TMU) as another aprotic solvent. It has a density of 0.972 at 15°C and boiling point of 177°C. The purpose was to study the effect of the substitution of the dimethylamino group for the hydrogen attached to the carbonyl group of dimethyl formamide. Thus TMU was examined to determine its dielectric constant, solvent power, viscosity and the conductance of its solutions. It was found that its dielectric constant was about 25 and its viscosity was 1.41 centipoises at 25°C. Among the solutes tested in TMU, the one molal solution of cesium hexafluorophosphate showed the best conductivity, $2.6 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$.

A number of fluorine-containing and chlorine-containing compounds were added to the list of solutes and the conductivities of some

of their solutions in DMF, PC and TMU were measured.

All the results of the screening tests are presented in Table I. (Pages IV-1 through 9).

The examination of Table I reveals that most of the one molal solutions had conductivities higher than that of solutions which became saturated at a concentration of less than one molal. In other words, the solutions with higher concentration of solutes gave higher conductances than the saturated solutions.

2. Quantitative Studies. The solutions for the quantitative determination of concentration-conductivity relationships were prepared by mixing the solute and the solvent at various concentration levels. Conductivity measurements were then made. Visual observation of undissolved solids supplemented by the conductivity measurements enabled us to determine the concentration at saturation.

The following systems were tested:

- a. KPF_6 - Dimethyl formamide.
- b. NaBF_4 - Dimethyl formamide.
- c. NaPF_6 - Dimethyl formamide.
- d. KPF_6 - Propylene carbonate.
- e. NaBF_4 - Propylene carbonate.

a. KPF_6 -DMF (Table II page IV-10 and Figure 1 page IV-11).

The solubility of KPF_6 in DMF exceeded four molal and the maximum conductivity-- $2.48 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$ --existed at 1.5 molal concentration. It was felt that the decrease in conductivity as the concentration exceeds 1.5 molal level was due to the increase in viscosity. The viscosities were then measured by using Ostwald-type viscosimeters at 25°C (the apparatus is shown in Figure 2 page IV-12). The results show that as the concentration exceeded 1.5 molal, the viscosity increased drastically. This phenomenon may have resulted from the interaction of the solute ions with the solvent.

b. NaBF_4 -DMF (Table III page IV-13).

The solubility of NaBF_4 in DMF was high. It was noted that a certain small amount of solid was present at the bottom of each of the solutions at all concentrations. The amount of the insoluble solid was estimated*to be 8 to 11% by weight of the total amount of solute added to the DMF and its identity has not yet been determined. The maximum conductivity-- $2.27 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$ --existed at 1.48 molal (not corrected for the insoluble solid).

Although the concentrations have not yet been corrected for the insoluble residue, the shape of the conductivity curve should not be changed by the correction.

* The solution and the solid were filtered and washed with DMF. The solid was then dried and weighed.

c. NaPF_6 -DMF (Table IV page IV-14).

In this system an insoluble residue was also present. The estimated amount of insoluble solid is about 13% by weight of the total solute added to the DMF. At 1.5 molal concentration where maximum conductivity should have been observed, a point off of the curve was obtained and the recheck of the point has not as yet been made, and will be established later.

d. KPF_6 -PC (Table V page IV-15).

At a concentration of about one molal the solution became saturated and exhibited a maximum conductivity of $7.25 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$. It appears therefore that the conductivity is limited by the solubility.

e. NaBF_4 -PC (Table VI page IV-16).

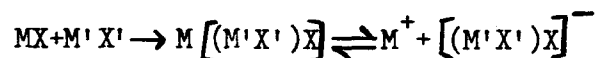
Again, there was a certain amount of insoluble solid present in each solution. Since both the maximum conductivity, $1.77 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$, and the solubility (less than 1 molal) are low, the amount of the insoluble solid was not estimated.

To summarize the findings from the above quantitative studies, it was noted that the propylene carbonate solutions did not exhibit maximum conductivity at a concentration lower than the saturation point. It appears that the solubilities of KPF_6 and NaBF_4 in PC were not high enough to allow the conductivities to

exceed the maxima. As for the DMF solutions, maximum conductivities existed at concentrations lower than the saturation points. The high degree of interaction of the solute ions apparently accounts for the decrease in conductance at higher concentrations.

3. Exploratory Tests.

- a. Mixed Solutes. Two salts may react and form ionizable complexes which can dissociate in the solution and form free ions according to the following reactions:



If the products are easier to ionize in a solvent than either MX or M'X', the synergistic effect should be detectable by means of the conductivity measurement. Furthermore it was felt that the order of addition of the two salts to the solvent might influence the nature of the reaction involving three reactants, i.e. MX, M'X' and the solvent. Therefore, the conductivity measurements were repeated for some of the MX-M'X'-solvent systems by reversing the order of addition of these two salts.

The results are presented in Table I pages IV-2, 3, 4 and 7. It was found that in most cases the conductivities were unfavorable, although the BeCl₂-SiF₄-DMF system exhibited a synergistic effect. The order of addition of the salts did not affect the conductivity significantly.

b. Salt-Ether Complexes. It is known that ether-oxygen is an electron donor, and Lewis acids are electron acceptors. They are capable of forming coordination compounds. The coordinate covalent bonds between the metal of the Lewis acid and the electron donor may be very strong as compared with the ionic bond between the metal of Lewis acid and the anions of the Lewis acid. It should also be true that the stability of the metal chelate is the highest if the metal chelate is formed in such a way that the coordination number of the metal equals the number of the ligand groups (ether-oxygen) in the ether. If a suitable solvent is used to perform charge separation, i.e. to separate the large metal chelate cations from the anions of the Lewis acid, high ion concentrations may be obtained and this then might result in a very highly conductive solution. For this reason, we have selected a group of ethers (Table VII page IV-17) to be used in the conductivity tests.

Two ethers, m-dimethoxybenzene and Bis[2-(2-methoxy ethoxy) ethyl] ether, were tested with BeF_2 , BeCl_2 , BF_3 and BCl_3 .

Except for BeF_2 , all of the other solutes reacted exothermically with the ethers and resulted in colored solutions. The conductivity results are presented in Table VIII page IV-18. The solutions tested thus far are all too low in conductivity to be used as electrolytes.

c. Tetrabutyl ammonium iodide (TBAI)-Solvent.

TBAI has both large anions and cations and was originally selected to study the effect of ionic size of solute on solubility and conductivity. Its one molal solution in PC had a conductivity of $5.3 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$ which is fairly high among the PC solutions but not as high as the value obtained in its DMF solution. It was then felt that the effect of the low viscosity of DMF might be more significant than the effect of the high dielectric constant of PC. Two more solvents, i.e. N-methyl formamide (NMF) and TMU, were then tested with TBAI as the solute. The conductivities of the solutions and the dielectric constants and viscosities of the solvents are presented as follows:

<u>Solvent</u>	<u>Solvent Properties</u>		<u>Solution</u>	
	<u>Dielectric Constant</u>	<u>Viscosity (Centipoises)</u>	<u>Specific Conductance ($\text{ohm}^{-1} \text{ cm}^{-1}$)</u>	
NMF	182	1.88	1.2×10^{-2}	1 molal solution
PC	64	2.52	0.53×10^{-2}	1 molal solution
DMF	37	0.81	1.0×10^{-2}	1 molal solution
TMU	25	1.41	0.18×10^{-2}	Saturated at less than 1 molal

The results suggest that the influence of the viscosity on the conductivity may be just as important as that of the dielectric constant.

d. Alkali metal hexafluorophosphates-DMF solutions. Cesium, potassium, sodium and lithium hexafluorophosphates were

selected to study the effect of size of alkali metal cations on the conductivities. All the hexafluorophosphates tested were very soluble in DMF. The conductivities of the one molal solutions were measured and tabulated below:

CsPF ₆	2.52×10^{-2}	(26°C)
KPF ₆	2.37×10^{-2}	(27°C)
NaPF ₆	2.33×10^{-2}	(29°C)
* LiPF ₆	2.06×10^{-2}	(28.5°C)

It appears that the conductivity increases slightly with increasing cation size but that the conductivity might be dominated by the hexafluorophosphate anion.

B. Electrochemical Tests.

As a preliminary study of the characteristics of the electrode materials in the more promising electrolytes, the electrochemical

* We were unable to purchase pure anhydrous LiPF₆. Therefore, it was prepared metathetically by mixing a two-molal KPF₆-DMF solution and a two-molal LiCl-DMF solution in the proper ratio. Previous conductivity measurements had indicated a low solubility of KCl in DMF. As expected, a white crystalline solid precipitated when the above two solutions were mixed. This solid was filtered, washed with DMF, weighed, and analyzed. The results were as follows:

	<u>Theoretical KCl</u>	<u>KCl found</u>	
Total weight	7.04 gm	7.05 gm	
Weight % K	53.2	53.3	(flame photometer)
Weight % Cl	46.8	45.6	(volhard titration)
Weight % Li	0.0	<0.05	(flame photometer)

Thus we conclude that the conversion of KPF₆ and LiCl to LiPF₆ and KCl was about 98%.

tests on small cells were performed using NiF_2 -Ni and CuF_2 -Cu as the cathode materials and Mg as the anode material. The electrodes and the electrolytes were desiccated over P_2O_5 for at least two days prior to the tests. The objectives of the qualitative electrochemical tests were to determine, 1) if the cell systems exhibit the theoretical open circuit potentials, and, 2) the compatibility of the electrode materials and the electrolytes. The results are presented in Table IX page IV-19 through 20.

The initial open circuit potentials of all the systems tested were far below the theoretical values. Charging current was then applied to the cell systems to reduce the magnesium surface and also to remove moisture electrochemically. In most cases, the observed open circuit potentials after charging were higher than the theoretical values (see table below).

<u>Cell Systems</u>	<u>Highest Values Obtained: OCV (volts)</u>		<u>Theoretical OCV (volts)</u>
	<u>Initial</u>	<u>After Charging</u>	
1. Mg/ KPF_6 -PC/ CuF_2 -Cu	1.36	1.114	2.92
2. Mg/ NaBF_4 -PC/ CuF_2 -Cu	1.31	3.0	2.92
3. Mg/ KPF_6 -PC/ NiF_2 -Ni	1.24	3.14	2.21
4. Mg/ NaBF_4 -PC/ NiF_2 -Ni	1.24	2.9	2.21
5. Mg/ KPF_6 -DMF/ NiF_2 -Ni	1.20	3.26	2.21
6. Mg/ NaBF_4 -DMF/ NiF_2 -Ni	1.22	2.42	2.21

The number "1" system was run before the others and the charging period was short as compared with that of the other experiments. Had a longer charging period been used, a higher open circuit potential than 1.44 volts might have been obtained. In the other experiments where abnormally high open circuit potentials were obtained, longer charging periods were used.

Visual observations were frequently made during the tests. No significant corrosion of the magnesium anode was observed and the cathode materials appeared to be stable in all of the six systems tested.

The system $\text{Mg/KPF}_6\text{-PC/NiF}_2\text{-Ni}$ was selected to study the effect of moisture on the cell potential by using a $\text{KPF}_6\text{-PC}$ solution already exposed to the moist atmosphere for two days. It was found that the high open circuit potential was never achieved and the measured open circuit potentials were unstable.

Another set of Mg and $\text{NiF}_2\text{-Ni}$ electrodes and $\text{KPF}_6\text{-PC}$ electrolytes which had been desiccated over P_2O_5 for some time were then assembled. The open circuit potential was at a level of 1.4 volts 30 minutes later. Charging current was then applied to the system and a gray material plated out on the surface of Mg anode. No gas bubbles were observed. A stable open circuit potential of 3.1 volts was then obtained. A fresh strip of Mg was placed in the solution and the potential of this strip against the charged cathode was found to be 1.45 volts. It is evident that the potential of the cathode apparently had not changed significantly. Thus the large

increase in cell potential is most likely attributable to a more active anode as a result of the charging process. We have no definite explanation of this phenomenon as yet. The curves (Figure 3 page IV-21) demonstrate the various effects discussed above,

The qualitative electrochemical test results indicate that:

- a. Extreme care in reduction of the moisture content in the cell systems is necessary to obtain the best results.
- b. The true cathode reaction mechanism may be different from the proposed cathode reaction from which the theoretical open circuit potential was calculated.
- c. The abnormally high OCV after charging was probably due to the presence of foreign species other than Mg on the anode. We believe it to be potassium or sodium but this will have to be confirmed experimentally.

II. CURRENT PROBLEMS

Our current problem still is to achieve levels of electrolyte conductivity well above $10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$. Our approach to solution thereof will be by striving to maximize the solubility of the ionizable solutes, while striving also to minimize the viscosity. The use of solutes with organic cations and large anions may aid in the first, while the use of mixed solvents may assist in the second.

III. WORK TO BE PERFORMED
DURING THE NEXT PERIOD

A. Next Quarter:

1. Continued screening of new electrolyte systems such as quaternary ammonium salts, complex salts, etc.
2. Quantitative studies of the effect of the concentration of solutes on the specific conductance and viscosity.
3. Mixed solvent effects on solubility, viscosity, and conductance.
4. Small cell tests to evaluate electrode material reversibility in the most promising electrolytes.
5. Stability tests of separator materials in the pure solvents.
6. Exploration of possible new solvents and organic solutes.

B. Next Month:

1. Continued qualitative screening of electrolyte systems.
2. Continued quantitative study of more promising electrolyte systems - emphasizing quaternary ammonium salts.
3. Study of the effect of mixed solvents to obtain further evidence of the relative importance of viscosity and dielectric constant.

TABLE I. SPECIFIC CONDUCTANCE OF SOLUTIONS
AT ROOM TEMPERATURE (25°-28°C)

- a. PROPYLENE CARBONATE.....Pages IV-1, IV-2, IV-3, IV-4
- b. DIMETHYL FORMAMIDE.....Pages IV-5, IV-6, IV-7
- c. TETRAMETHYL UREA.....Page IV-8
- d. N-METHYL FORMAMIDE.....Page IV-9

* * * * *

- NOTES: 1) All tests were made in a dry argon atmosphere.
- 2) All solutions are saturated at less than one molal concentration, unless marked otherwise.

TABLE I. SPECIFIC CONDUCTANCE OF SOLUTIONS
AT ROOM TEMPERATURE (25°C-28°C)

a. POLYETHYLENE CARBONATE

Solute	Specific Conductance ($\text{ohm}^{-1} \text{cm}^{-1}$)		Visual Observations		
	1 Day Exposure	2-3 Day Exposure	Solution	Solid	Others
Blank 1	1.42×10^{-5}	---	---	---	---
Blank 2	8.65×10^{-6}	9.52×10^{-6}	---	---	---
CsCl	8.48×10^{-5}	1.05×10^{-4} (31°C)	Clear	White	---
FeCl ₃	6.10×10^{-3}	6.30×10^{-3}	Red-brown	Dark brown	---
K ₂ BeF ₄	3.03×10^{-5}	3.04×10^{-5}	Clear	White	---
KCl	2.63×10^{-5}	2.81×10^{-5}	Clear	White	---
KPF ₆	7.70×10^{-3}	7.71×10^{-3}	Clear	White	---
LiPF ₆ ·H ₂ O	a) 3.70×10^{-4}	1.4×10^{-3}	Clear	White	---
	b) 6.72×10^{-4}	1.5×10^{-3}	Clear	White	---
LiSO ₃ F	2.52×10^{-4}	2.4×10^{-4}	Clear	White	---
Li ₂ SiF ₆	8.63×10^{-5}	8.9×10^{-5}	Clear	White	---
MgF ₂	1.48×10^{-5}	1.47×10^{-5}	Clear	White	---
MgCl ₂	7.90×10^{-4}	1.13×10^{-3}	Clear	White	---
Na ₃ AlF ₆	1.04×10^{-5}	1.02×10^{-5}	Clear	White	---

TABLE I. SPECIFIC CONDUCTANCE OF SOLUTION;
AT ROOM TEMPERATURE (25°C-28°C) - Continued

a. POLYPROPYLENE CARBONATE - Continued

Solute	Specific Conductance ($\text{ohm}^{-1} \text{cm}^{-1}$)		Visual Observations	
	1 Day Exposure	2-3 Day Exposure	Solution	Solid Others
NaCl	1.69×10^{-5}	1.65×10^{-5}	Clear	White ----
NaPF ₆	5.94×10^{-3}	7.55×10^{-3}	Clear	Tan ----
* TBAI	5.28×10^{-3}	5.25×10^{-3}	Clear yellow	---- ----
TiF ₃	3.69×10^{-4}	3.67×10^{-4}	Brown	Dark brown ----
TiF ₄	2.72×10^{-3}	3.54×10^{-3}	Brown	Tan ----
1 Hour Exposure				
AlF ₃ +RbF	7.62×10^{-5}	2.1×10^{-4}	Clear	White (1.45 molal RbF mix) ----
AlF ₃ +MgF ₂	1.38×10^{-5}	1.27×10^{-5}	Clear	Gray ----
* AlCl ₃	8.05×10^{-3} (33°C)	---	Brown	--- Exothermic
AlCl ₃ +CsF	7.70×10^{-3}	7.53×10^{-3}	Dark brown	Gray ----
AlCl ₃ +MgF ₂	6.70×10^{-3}	6.63×10^{-3}	Dark brown	Gray ----
AlCl ₃ +KCl	7.58×10^{-3}	8.64×10^{-3}	Dark brown	--- ----
AlCl ₃ +LiCl	7.28×10^{-3}	6.75×10^{-3}	Dark brown	Gray ----
AlCl ₃ +MgCl ₂	7.36×10^{-3}	6.70×10^{-3}	Dark brown	Gray ----

TBAI = tetra n-butylammonium iodide
* One molal solutions

TABLE I. SPECIFIC CONDUCTANCE OF SOLUTIONS
AT ROOM TEMPERATURE (25°C-28°C) - Continued

a. PROPYLENE CARBONATE - Continued

Solute	Specific Conductance ($\text{ohm}^{-1} \text{ cm}^{-1}$)		Visual Observations		
	1 Hour Exposure	2-3 Day Exposure	Solution	Solid	Others
$\text{BeF}_2 + \text{CsF}$	1.10×10^{-4}	3.59×10^{-4}	Clear	Gray	(0.54 molal CsF mix)
$\text{BeF}_2 + \text{RbF}$	7.34×10^{-5}	2.05×10^{-4}	Clear	Gray	---
$\text{BeF}_2 + \text{LiCl}$	1.07×10^{-4}	4.14×10^{-4}	Cloudy	White	---
$\text{BeF}_2 + \text{MgCl}_2$	1.44×10^{-4}	5.36×10^{-4}	Cloudy	Gray	---
BeCl_2	6.90×10^{-4}	---	Light green	Light green	Exothermic
$\text{BeCl}_2 + \text{CsF}$	5.16×10^{-4}	3.03×10^{-4}	Dark brown	Gray	---
$\text{BeCl}_2 + \text{MgF}_2$	9.20×10^{-4}	3.39×10^{-4}	Gray	Gray	---

BF_3 or SiF_4 gas was bubbled through the following solutions until a maximum conductivity was obtained. These solutions were all unsaturated with respect to BF_3 or SiF_4 , but saturated with respect to the solid solute except for AlCl_3 , which was 1 molal in concentration.

		1 Day Exposure		
BF_3	4.43×10^{-4} (32°C)	---	Brown	Exothermic
$\Delta \text{BF}_3 + \text{NaF}$	6.38×10^{-4}	---	Brown	Tan
SiF_4	4.50×10^{-4}	6.70×10^{-5}	Light yellow	Slightly Exothermic
$\Delta \text{SiF}_4 + \text{AlCl}_3$	---	6.52×10^{-3}	Brown	Exothermic

Δ Solutes were added to solvent in order shown

TABLE I. SPECIFIC CONDUCTANCE OF SOLUTIONS
AT ROOM TEMPERATURE (25°C-28°C) - Continued

a. PROPYLENE CARBONATE - Continued

Solute	Specific Conductance ($\text{ohm}^{-1} \text{ cm}^{-1}$)		Visual Observations		
	1 Hour Exposure	1 Day Exposure	Solution	Solid	Others
$\Delta \text{SiF}_4 + \text{BeCl}_2$	8.62×10^{-4}	5.48×10^{-4}	Light green	Green	Exothermic
$\Delta \text{SiF}_4 + \text{RbF}$	3.96×10^{-4}	1.27×10^{-4}	Clear	White	(1.48 molal RbF mix)
$\Delta \text{SiF}_4 + \text{TiF}_4$	3.61×10^{-3}	3.38×10^{-3}	Tan	Tan	---
$\Delta \text{AlCl}_3 + \text{SiF}_4$	7.98×10^{-3}	6.81×10^{-3}	Brown	---	Exothermic
$\Delta \text{BeCl}_2 + \text{SiF}_4$	6.83×10^{-4}	6.29×10^{-4}	Light green	Light green	---
$\Delta \text{KPF}_6 + \text{SiF}_4$	7.83×10^{-3}	7.80×10^{-3}	Clear	White	---

Δ Solutes were added to solvent in order shown

TABLE I. SPECIFIC CONDUCTANCE OF SOLUTIONS
AT ROOM TEMPERATURE (25°C-28°C) - Continued

b. DIMETHYL FORMAMIDE

Solute	Specific Conductance ($\text{ohm}^{-1} \text{cm}^{-1}$)		Visual Observations		
	1 Day Exposure	2-3 Day Exposure	Solution	Solid	Others
Blank 1	2.16×10^{-6}	---	---	---	---
Blank 2	1.89×10^{-6}	1.94×10^{-6}	---	---	---
AgF	3.04×10^{-5}	5.92×10^{-4}	Dark brown	Brown	---
AlCl ₃	3.11×10^{-3}	---	White milky	---	---
BeCl ₂	1.71×10^{-3}	---	Light green	White	Exothermic
CsCl	2.34×10^{-4}	2.94×10^{-4} (31°C)	Clear	White	---
* CsPF ₆	2.52×10^{-2}	---	Clear	---	---
* FeCl ₃	9.97×10^{-3}	1.21×10^{-2} (30°C)	Brown	---	Exothermic
FeCl ₃ +LiF	9.88×10^{-3}	Solidified	Brown	Yellow	Exothermic
K ₂ BeF ₄	1.05×10^{-4}	1.15×10^{-4}	Clear	White	---
KCl	1.48×10^{-4}	1.78×10^{-4}	Clear	White	---
* KI	2.22×10^{-2}	---	Clear	---	---
* KPF ₆	---	2.37×10^{-2}	Clear	---	---
* LiPF ₆	---	2.06×10^{-2}	Clear	---	---
LiPF ₆ ·H ₂ O	6.25×10^{-4}	9.77×10^{-4}	Clear	White	---
Li ₂ SiF ₆	9.97×10^{-4}	1.12×10^{-3}	Clear	White	---

* One molal solutions

TABLE I. SPECIFIC CONDUCTANCE OF SOLUTIONS
AT ROOM TEMPERATURE (25°C-28°C) - Continued

b. DIMETHYL FORMAMIDE - Continued

Solute	Specific Conductance ($\text{ohm}^{-1} \text{cm}^{-1}$)		Visual Observations		
	1 Day Exposure	2-3 Day Exposure	Solution	Solid	Others
LiSO_3F	1.97×10^{-3}	1.98×10^{-3}	Clear	White	---
MgCl_2	9.70×10^{-3}	1.00×10^{-2}	Clear	White	---
Na_3AlF_6	3.53×10^{-5}	3.68×10^{-5}	Clear	White	---
NaCl	---	3.74×10^{-4}	Clear	White	---
* NaPF_6	2.22×10^{-2}	2.22×10^{-2}	Tan	Tan	Exothermic
SnF_2	1.66×10^{-4}	1.72×10^{-4}	Clear	White	---
SnF_4	6.52×10^{-5}	8.25×10^{-5}	Clear	Gray	---
* TBAI	1.06×10^{-2}	1.06×10^{-2}	Clear	---	---
TlF_3	7.71×10^{-5}	9.48×10^{-5}	Brown	Brown	---
TlF_4	1.98×10^{-4}	2.69×10^{-4}	Clear	White	---
TlF	1.83×10^{-5}	3.99×10^{-5}	Clear	White	---
BF_3	1.02×10^{-2}	---	Clear	---	Exothermic
SiF_4	5.35×10^{-4} (24 Hr.)	---	Clear	---	Exothermic

BF_3 or SiF_4 gas was bubbled through the following solutions until a maximum conductivity was obtained. These solutions were all unsaturated with respect to BF_3 or SiF_4 , but saturated with respect to the solid state.

1 Hour Exposure

TBAI = tetra n-butylammonium iodide
* One molal solutions

TABLE I. SPECIFIC CONDUCTANCE OF SOLUTIONS
AT ROOM TEMPERATURE (25°C-28°C) - Continued

b. DIMETHYL FORMAMIDE - Continued

Solute	Specific Conductance ($\text{ohm}^{-1} \text{cm}^{-1}$)		Visual Observations	
	1 Hr. Exposure	2-3 Day Exposure	Solution	Others
$\Delta \text{SiF}_4 + \text{AlCl}_3$	8.65×10^{-3}	9.85×10^{-4}	Clear	White Exothermic
$\Delta \text{SiF}_4 + \text{BeCl}_2$	4.88×10^{-3}	5.49×10^{-3}	Light green	White Exothermic
$\Delta \text{SiF}_4 + \text{RbF}$	7.44×10^{-4}	6.03×10^{-4}	Clear	White (1.45 molar RbF mix) Exothermic
$\Delta \text{SiF}_4 + \text{TlF}_4$	7.26×10^{-4}	9.36×10^{-4}	Clear	White Exothermic
$\Delta \text{BeCl}_2 + \text{SiF}_4$	4.93×10^{-3}	5.72×10^{-3}	Green	White Exothermic
$\Delta \text{KPF}_6 + \text{SiF}_4$	2.59×10^{-2}	2.24×10^{-2}	Clear	White Exothermic

Δ Solutes were added to solvent in order shown

TABLE I. SPECIFIC CONDUCTANCE OF SOLUTIONS
AT ROOM TEMPERATURE (25°-28°C) - Continued

c. TETRAMETHYL UREA

Solute	Specific Conductance ($\text{ohm}^{-1} \text{cm}^{-1}$)		Visual Observations		
	1 Day Exposure	2-3 Day Exposure	Solution	Solid	Others
Blank	1.84×10^{-6}	---	---	---	---
* CsPF_6	2.60×10^{-2}	---	Clear	---	---
FeCl_3	2.44×10^{-3}	2.40×10^{-3}	Brown	Brown	---
* KPF_6	5.53×10^{-3}	5.45×10^{-3}	Clear	---	Exothermic
LiCl	---	6.48×10^{-3}	Clear	White	---
$\text{LiPF}_6 \cdot \text{H}_2\text{O}$	1.69×10^{-4}	3.33×10^{-4}	Clear	White	---
LiSO_3F	2.31×10^{-4}	3.48×10^{-4}	Clear	Gray	---
MgCl_2	3.32×10^{-4}	4.02×10^{-4}	Clear	White	---
MgSiF_6	6.18×10^{-4}	2.18×10^{-3}	Clear	White	---
NaBF_4	3.97×10^{-3}	4.83×10^{-3}	Clear	White	---
NaPF_6	6.77×10^{-3}	6.83×10^{-3}	Tan	Tan	Exothermic
TBAI	1.55×10^{-3}	1.78×10^{-3}	Clear	Cream	---

TBAI = tetra n-butylammonium iodide.

* One molal solutions

TABLE I. SPECIFIC CONDUCTANCE OF SOLUTIONS
AT ROOM TEMPERATURE (25°-28°C) - Continued

d. N-METHYL FORMAMIDE				
<u>Solute</u>	<u>Specific Conductance (ohm⁻¹ cm⁻¹)</u>		<u>Visual Observations</u>	
	<u>1 Day Exposure</u>	<u>2-3 Day Exposure</u>	<u>Solution</u>	<u>Solid</u> <u>Others</u>
Blank	5.30×10^{-3}	5.60×10^{-3}	---	---
* TBAI	1.17×10^{-2}	1.23×10^{-2} (31°C)	Clear	---

TBAI = tetra n-butylammonium iodide
* One molal solutions

TABLE II. PROPERTIES OF KPF₆-
DIMETHYL FORMAMIDE SOLUTIONS

<u>m</u>	<u>η(25°C)</u>	<u>L</u>	
0.0109	0.840	0.0714×10^{-2}	(27°C)
0.0963	0.895	0.506×10^{-2}	(27°C)
0.498	1.206	1.73×10^{-2}	(27°C)
0.76	1.42	2.15×10^{-2}	(27°C)
0.99	1.68	2.36×10^{-2}	(27°C)
1.25	2.02	2.47×10^{-2}	(27°C)
1.50	2.51	2.48×10^{-2}	(27°C)
1.76	2.92	2.44×10^{-2}	(27°C)
2.19	3.52	2.31×10^{-2}	(27°C)
2.97	7.18	1.80×10^{-2}	(29°C)
3.99	14.7	1.20×10^{-2}	(28°C)

Symbols:

- m = concentration in molality
- η = viscosity in centipoises
- L = specific conductance in $\text{ohm}^{-1} \text{cm}^{-1}$

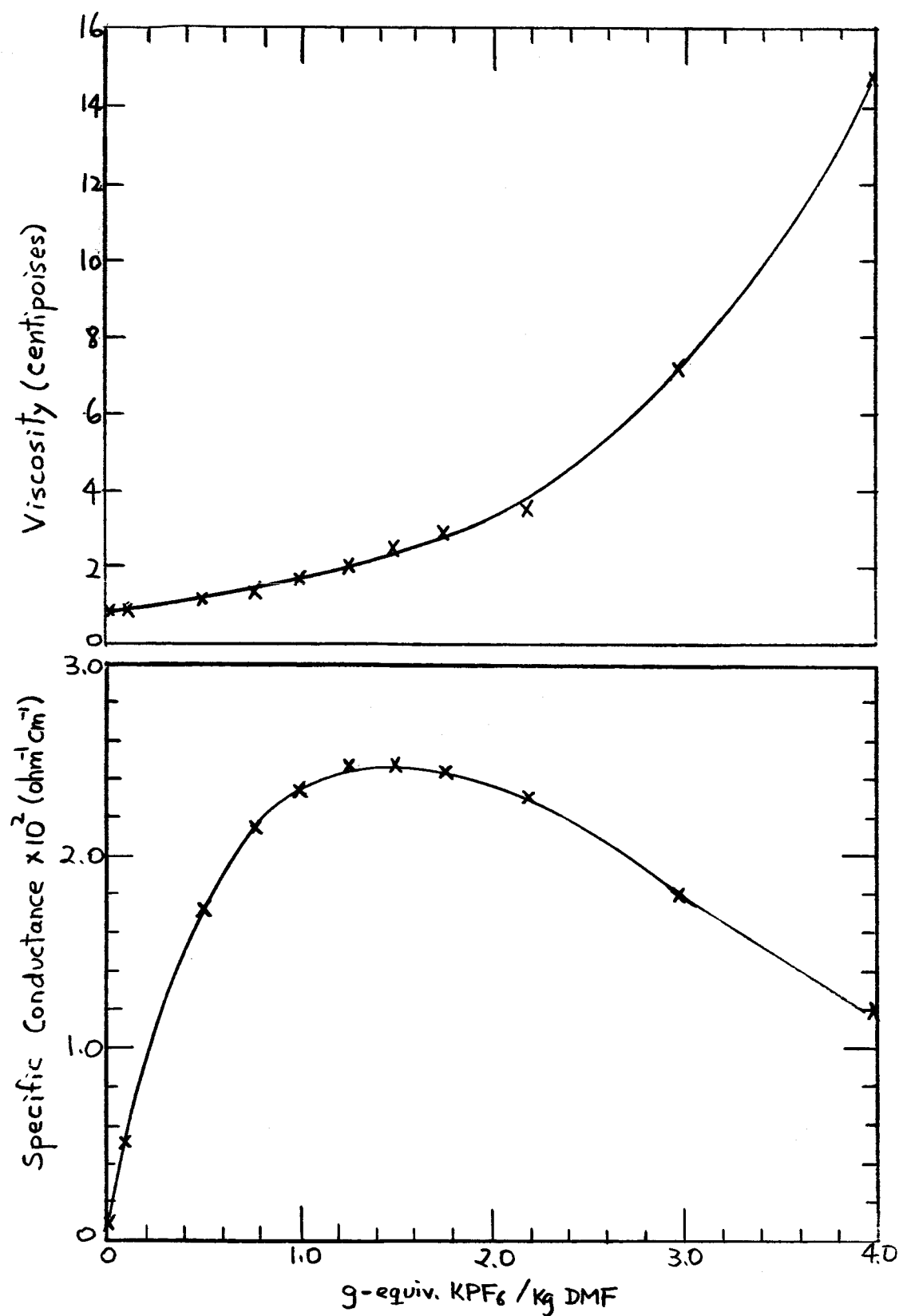


FIGURE 1. SPECIFIC CONDUCTANCE AND VISCOSITY
OF KPF₆-DMF SOLUTIONS

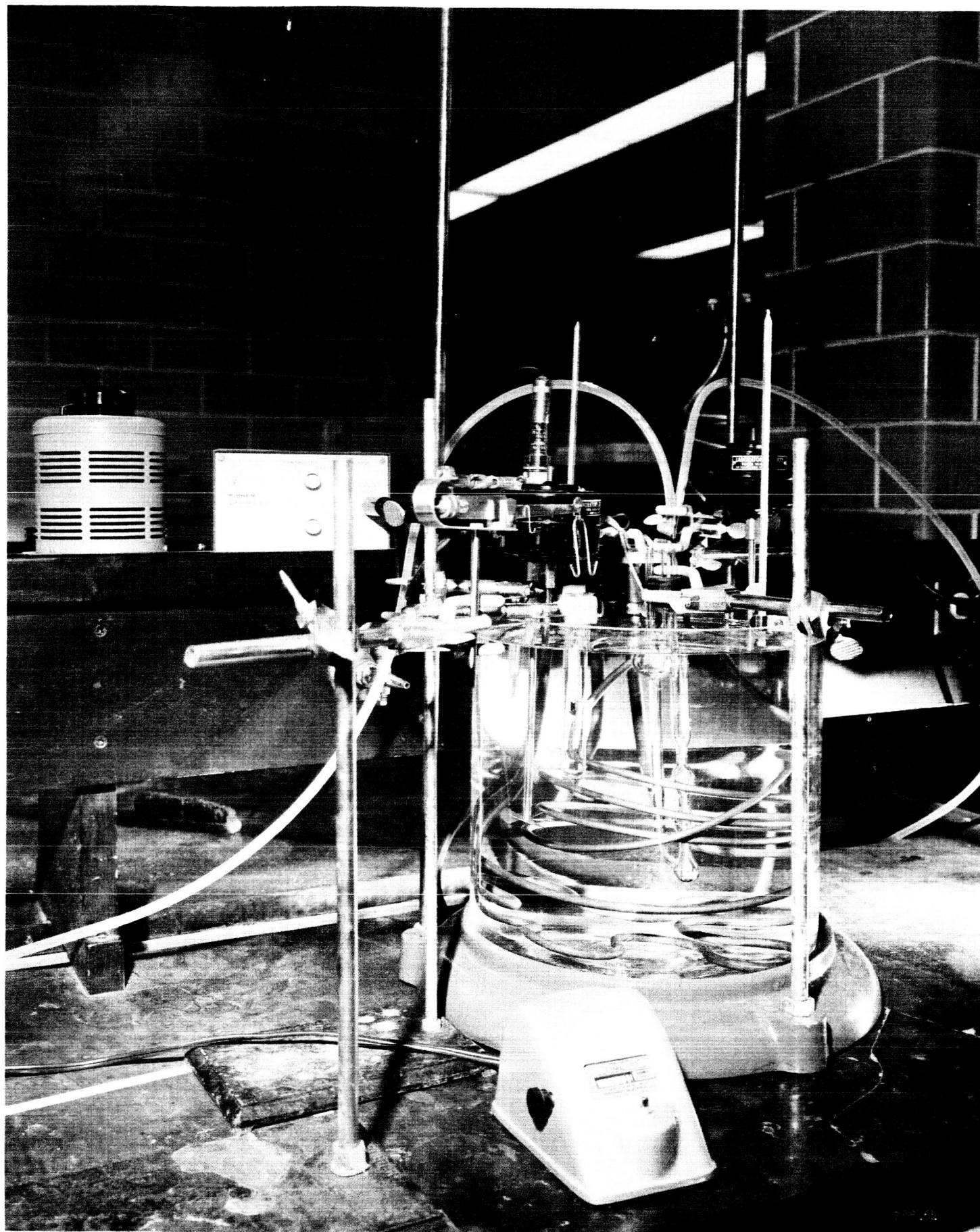


FIGURE 2. VISCOSITY APPARATUS
Page IV-12

TABLE III. ELECTROLYTIC CONDUCTANCE OF
NaBF₄-DIMETHYL FORMAMIDE SOLUTIONS

<u>m</u>	<u>L</u>	
0.0196	0.109×10^{-2}	(28°C)
0.174	0.715×10^{-2}	(29°C)
0.610	1.63×10^{-2}	(26°C)
1.01	2.04×10^{-2}	(27°C)
1.48	2.27×10^{-2}	(28°C)
1.92	2.17×10^{-2}	(28°C)
3.02	1.81×10^{-2}	(28°C)
4.12	1.33×10^{-2}	(28°C)

Symbols:

m = concentration in molality.
L = specific conductance in $\text{ohm}^{-1} \text{cm}^{-1}$.

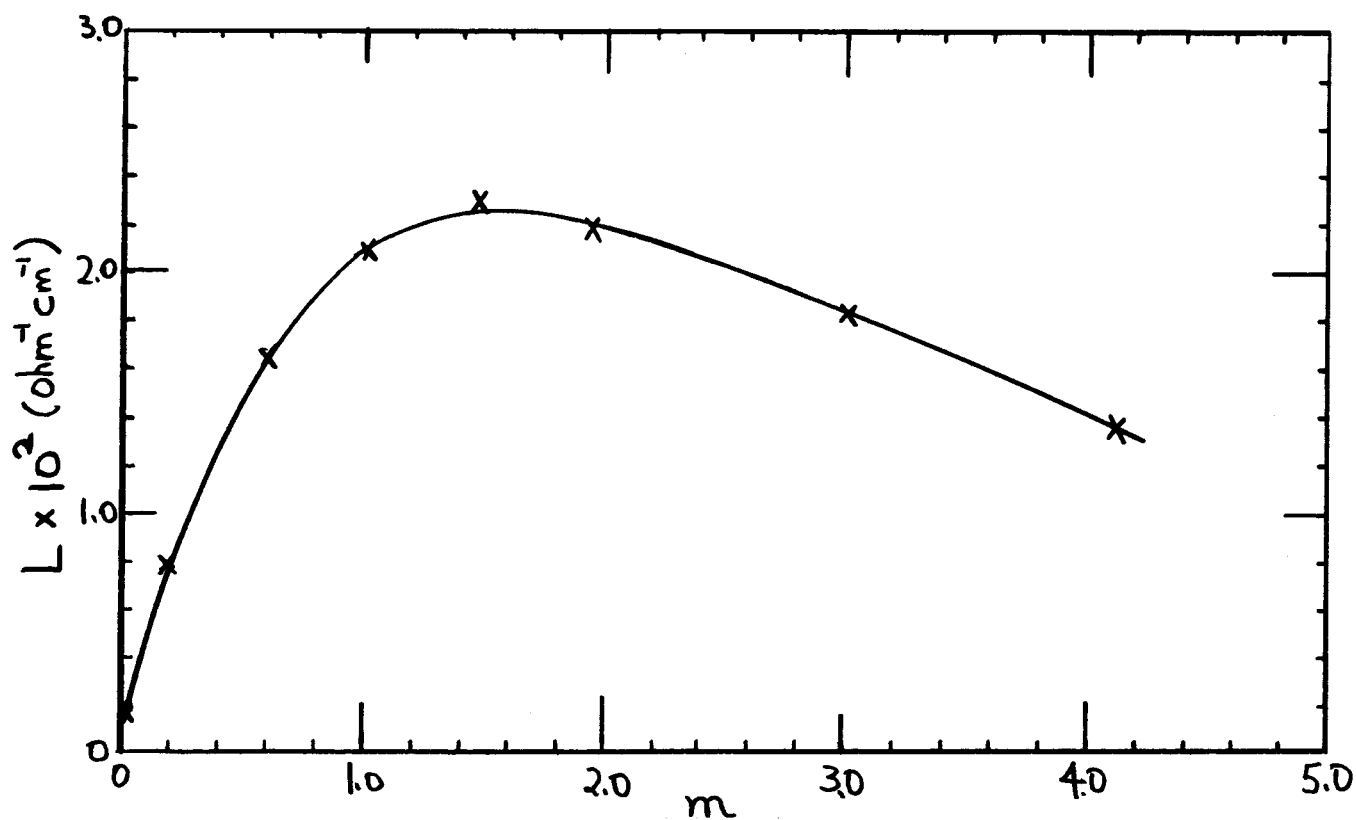


TABLE IV. ELECTROLYTIC CONDUCTANCE OF
 NaPF_6 - DIMETHYL FORMAMIDE SOLUTIONS

<u>m</u>	<u>L</u>	
0.401	1.42×10^{-2}	(27°C)
0.995	2.33×10^{-2}	(29°C)
1.496	2.31×10^{-2}	(27°C)
1.98	2.36×10^{-2}	(29°C)
2.36	2.00×10^{-2}	(27°C)
2.88	1.59×10^{-2}	(27°C)
4.02	0.475×10^{-2}	(29°C)

Symbols:

m = concentration in molality

L = specific conductance in $\text{ohm}^{-1} \text{cm}^{-1}$

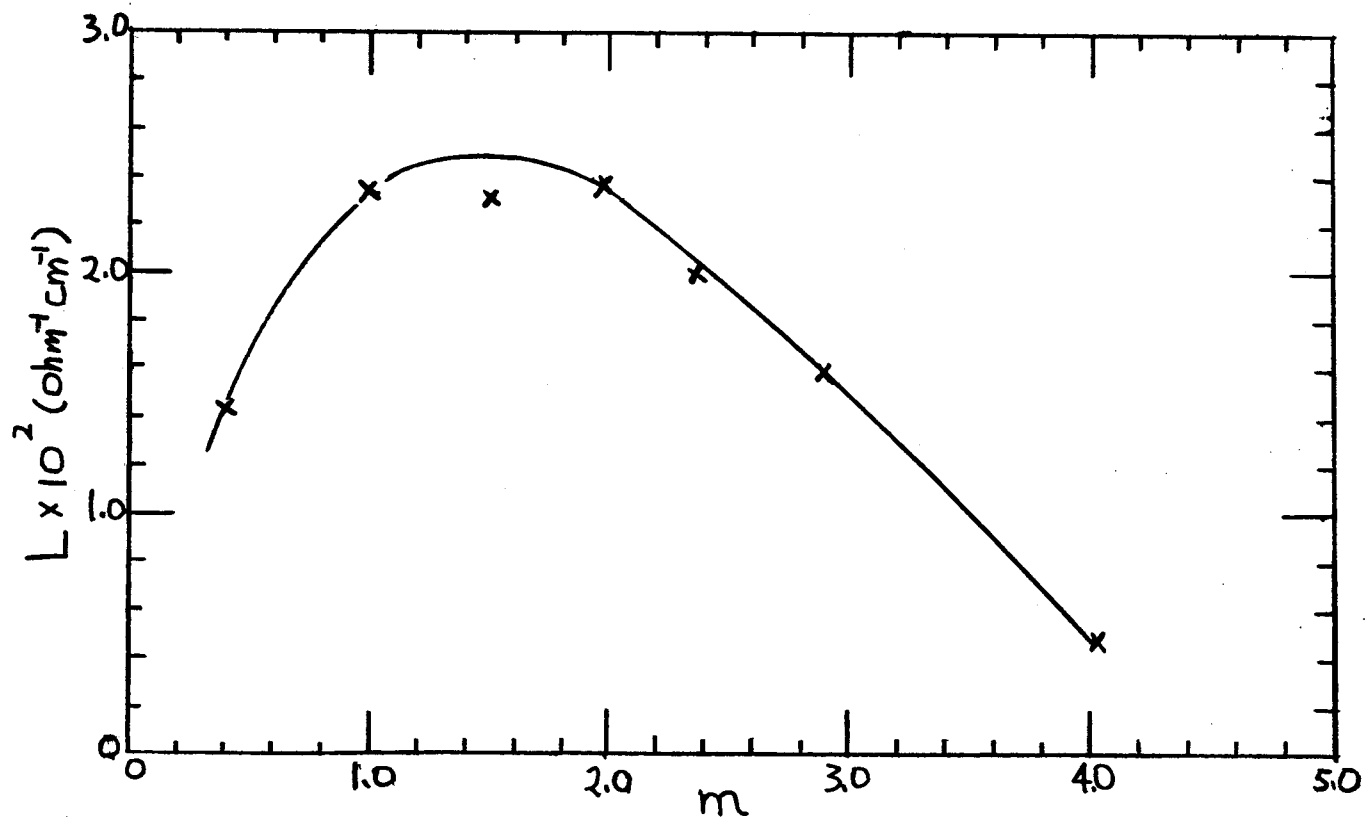


TABLE V. ELECTROLYTIC CONDUCTANCE OF
KPF₆-PROPYLENE CARBONATE SOLUTIONS

<u>m</u>	<u>L</u>		
1.40	7.29×10^{-3}	(25°C)	(Saturated)
1.20	7.30×10^{-3}	(25°C)	(Saturated)
1.00	7.24×10^{-3}	(25°C)	
0.80	7.19×10^{-3}	(25°C)	
0.603	6.78×10^{-3}	(25°C)	
0.40	5.78×10^{-3}	(25°C)	
0.216	4.11×10^{-3}	(25°C)	

Symbols:

m = concentration in molality

L = specific conductance in $\text{ohm}^{-1} \text{cm}^{-1}$

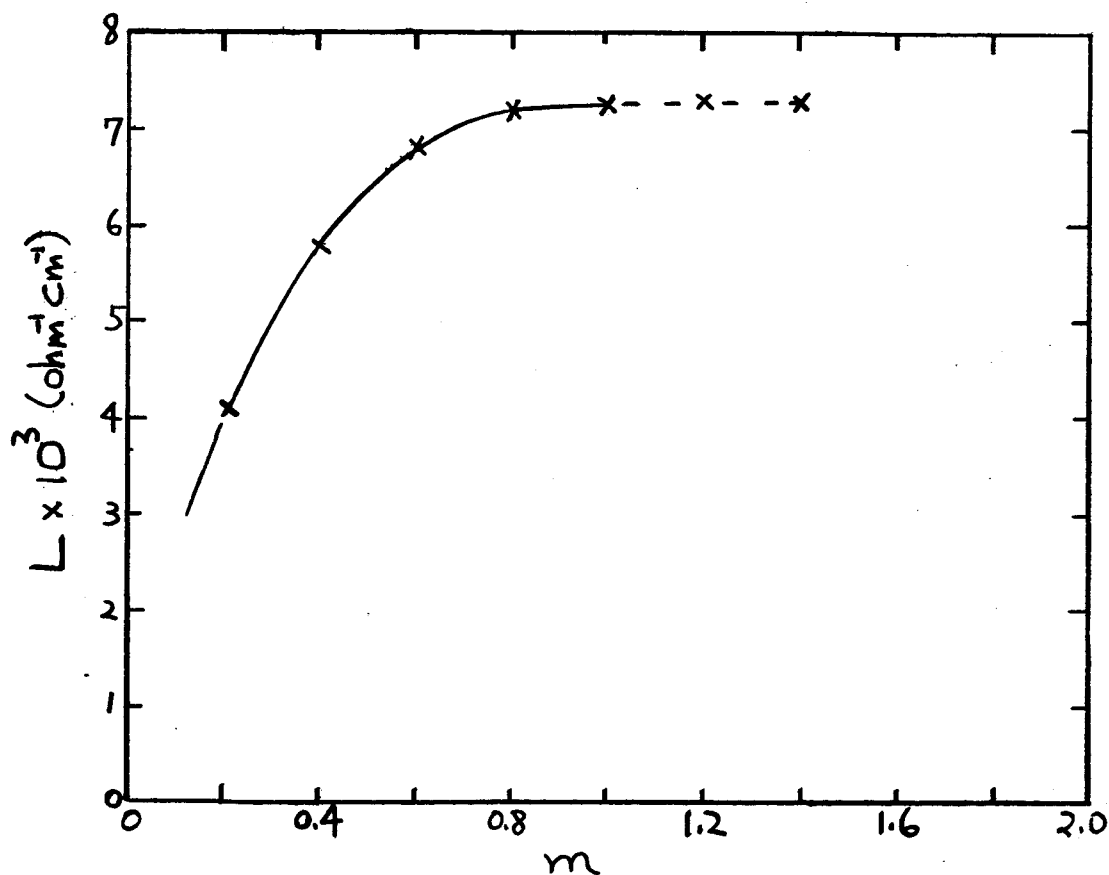


TABLE VI. ELECTROLYTIC CONDUCTANCE OF
NaBF₄-PROPYLENE CARBONATE SOLUTIONS

<u>m</u>	<u>L</u>		
1.40	1.78×10^{-3}	(28°C)	(Saturated)
1.205	1.77×10^{-3}	(28°C)	(Saturated)
1.005	1.77×10^{-3}	(28°C)	
0.603	1.64×10^{-3}	(28°C)	
0.400	1.54×10^{-3}	(28°C)	
0.200	1.42×10^{-3}	(28°C)	

Symbols:

m = concentration in molality

L = specific conductance in $\text{ohm}^{-1} \text{cm}^{-1}$

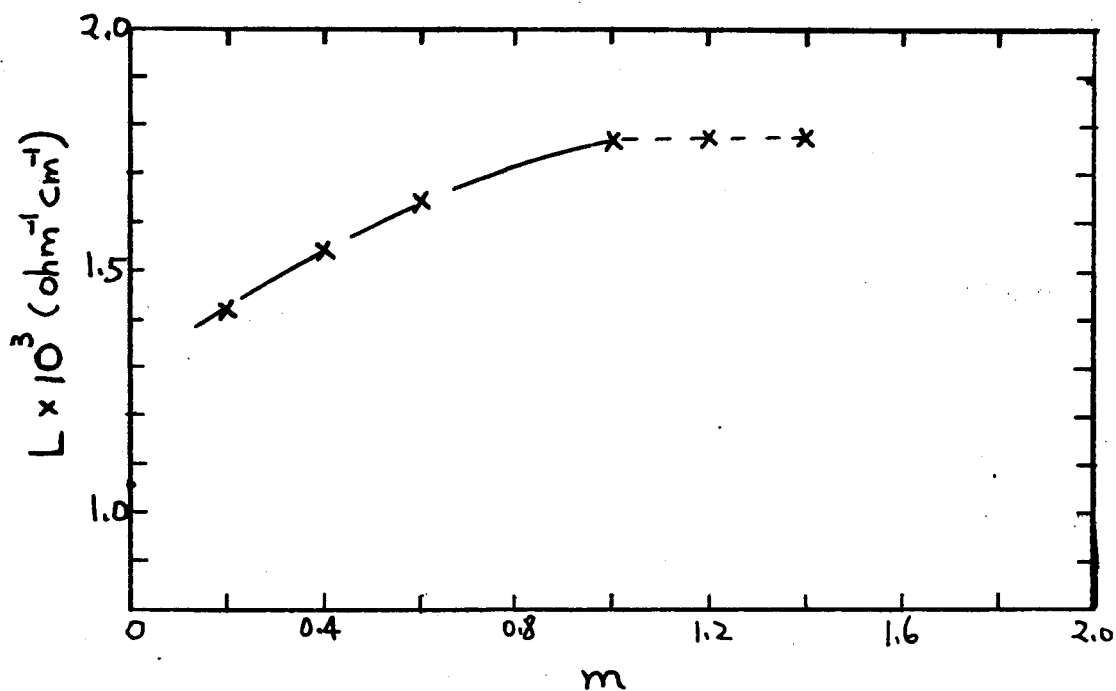


TABLE VII. SERIES OF ETHERS FOR
COORDINATION STUDIES



1) Diethyl ether	$\text{CH}_3\text{CH}_2\text{-O-CH}_2\text{CH}_3$
2) Methylal	$\text{CH}_3\text{-O-CH}_2\text{-O-CH}_3$
3) 1, 1-dimethoxyethane	$\text{CH}_3\text{-O-CH(CH}_3\text{)-O-CH}_3$
4) 1, 2-dimethoxyethane	$\text{CH}_3\text{-O-CH}_2\text{-CH}_2\text{-O-CH}_3$
5) m-dimethoxybenzene	$\text{CH}_3\text{-O-}$  -O-CH_3
6) p-dimethoxybenzene	$\text{CH}_3\text{-O-}$  -O-CH_3
7) Bis(2-ethoxyethyl)ether	$\text{CH}_3\text{CH}_2\text{-O-CH}_2\text{CH}_2\text{-O-CH}_2\text{CH}_2\text{-O-CH}_2\text{CH}_3$
8) 1, 2-Bis(methoxyethoxy) ethane	$\text{CH}_3\text{-O-CH}_2\text{CH}_2\text{-O-CH}_2\text{CH}_2\text{-O-CH}_2\text{CH}_2\text{-O-CH}_3$
9) Bis[2-(2-methoxyethoxy) ethyl] ether	$\text{CH}_3\text{-O-CH}_2\text{CH}_2\text{-O-CH}_2\text{CH}_2\text{-O-CH}_2\text{CH}_2\text{-O-CH}_2\text{CH}_2\text{-O-CH}_3$

TABLE VIII. FORMATION OF ETHER
COMPLEXES OF SOLUTES

M-DIMETHOXYBENZENE

<u>Solute</u>	<u>Specific Conductance</u> (ohm ⁻¹ cm ⁻¹)		<u>Observations</u>
	<u>1 Hr. Exposure</u>		
Blank 1	1.94 x 10 ⁻⁹		---
Blank 2	2.53 x 10 ⁻⁹		---
BeCl ₂	1.33 x 10 ⁻⁶ (31°C)		Yellow, exothermic reaction
BeF ₂	2.51 x 10 ⁻⁹ (27°C)		No apparent reaction
BCl ₃	3.24 x 10 ⁻⁴		Red, exothermic reaction
BF ₃	3.32 x 10 ⁻⁵ (42.5°C)		Orange color, exothermic reaction

BIS [2-(2-METHOXYETHOXY)ETHYL] ETHER

	<u>1 Hr. Exposure</u>	<u>24 Hr. Exposure</u>	
Blank 1	4.60 x 10 ⁻⁹	1.62 x 10 ⁻⁹	---
Blank 2	1.21 x 10 ⁻⁹	---	---
BeCl ₂	1.49 x 10 ⁻⁵ (38°C)	1.66 x 10 ⁻⁹	Brown, exothermic reaction
BeF ₂	1.77 x 10 ⁻⁷ (30°C)	1.27 x 10 ⁻⁹	Milky, slightly exothermic reaction
BCl ₃	2.64 x 10 ⁻⁹ (54°C)	---	Dark brown, exothermic reaction
BF ₃	1.91 x 10 ⁻⁹ (71°C)	---	Brown, exothermic reaction

Note: All samples were at room temperature (23°C-25°C) when specific conductivities were recorded unless specified otherwise.

TABLE IX. CELL POTENTIAL

<u>Reaction</u>	<u>E°</u>
$\text{Mg} + \text{CuF}_2 = \text{MgF}_2 + \text{Cu}$	2.92 volts
$\text{Mg} + \text{NiF}_2 = \text{MgF}_2 + \text{Ni}$	2.21 volts

1) Mg/KPF_6 -Propylene Carbonate (Sat.)/ CuF_2 -Cu

Initial OCV: rises to 1.36 volts in 10 minutes

OCV after charge at $36\mu\text{a}/\text{cm}^2$ for 6 min.: 1.38 volts

OCV after discharge at $20\mu\text{a}/\text{cm}^2$ for 70 min.: 0.84 volts

OCV after charge at $40\mu\text{a}/\text{cm}^2$ for 20 min.: 1.34 rises to 1.44 volts in 6 hrs.

OCV after discharge at $30\mu\text{a}/\text{cm}^2$ for 20 min.: 1.30 rises to 1.43 volts in 37 hrs.

2) Mg/NaBF_4 -Propylene Carbonate (Sat.)/ CuF_2 -Cu

Initial OCV: rises to 1.31 volts in 20 minutes

OCV after discharge at $90\mu\text{a}/\text{cm}^2$ for 30 min.: 1.31 volts

OCV after charge at $50\mu\text{a}/\text{cm}^2$ for 25 min.: 3.0 falls to 0.98 volts in 10 min.

OCV after charge at $1\text{ ma}/\text{cm}^2$ for 50 min.: 2.56 falls to 2.07 volts in 10 min.

OCV after charge at $1\text{ ma}/\text{cm}^2$ for 90 min.: 2.75 falls to 2.30 volts in 10 min.

OCV after charge at $1\text{ ma}/\text{cm}^2$ for 80 min.: 2.8 falls to 2.31 volts in 10 min.

3) Mg/KPF_6 -Propylene Carbonate (Sat.)/ NiF_2 -Ni

Initial OCV: rises to 1.24 volts in 30 minutes

OCV after discharge at $18\mu\text{a}/\text{cm}^2$ for 10 min.: 1.21 rises to 1.28 volts in 25 min.

OCV after charge at $2\text{ ma}/\text{cm}^2$ for 10 min.: 2.98 falls to 2.7 volts in 4 min.

OCV after charge at $2\text{ ma}/\text{cm}^2$ for 20 min.: 3.08 falls to 2.7 volts in 14 min.

OCV after charge at $2\text{ ma}/\text{cm}^2$ for 30 min.: 3.10 falls to 2.7 volts in 22 min.

OCV after charge at $2\text{ ma}/\text{cm}^2$ for 70 min.: 3.14 falls to 3.12 volts in 1 min.

TABLE IX. CELL POTENTIAL (Continued)

4) Mg/NaBF₄-Propylene Carbonate (Sat.)/NiF₂-Ni

Initial OCV: rises to 1.24 volts in 20 minutes

OCV after discharge at 40 μ a/cm² for 10 min.: 1.31 falls to 1.27 volts in 10 min.

OCV after charge at 1 ma/cm² for 10 min.: 2.15 falls to 1.44 volts in 10 min.

OCV after charge at 0.3 ma/cm² for 60 min.: 2.32 falls to 1.71 volts in 10 min.

OCV after charge at 0.2 ma/cm² for 160 min.: 2.9 falls to 1.85 volts in 10 min.

OCV after charge at 0.25 ma/cm² for 110 min: 2.03 volts

OCV after discharge at 25 μ a/cm² for 20 min.: 1.37 rises to 1.44 volts in 3 min.

5) Mg/KPF₆-Dimethyl Formamide (0.79 molal)/NiF₂-Ni

Initial OCV: 1.20 volts

OCV after discharge at 30 μ a/cm² for 10 min.: 1.06 rises to 1.16 volts in 30 min.

OCV after charge at 2 ma/cm² for 10 min.: 3.0 falls to 1.48 volts in 2 min.

OCV after charge at 1 ma/cm² for 40 min.: 3.1 falls to 1.68 volts in 2 min.

OCV after charge at 1 ma/cm² for 300 min.: 3.26 falls to 2.47 volts in 2 min.

6) Mg/NaBF₄-DMF (0.68 molal)/NiF₂-Ni

Initial OCV: 1.22 volts

OCV after discharge at 30 μ a/cm² for 10 min.: 1.23 falls to 1.13 volts in 10 min.

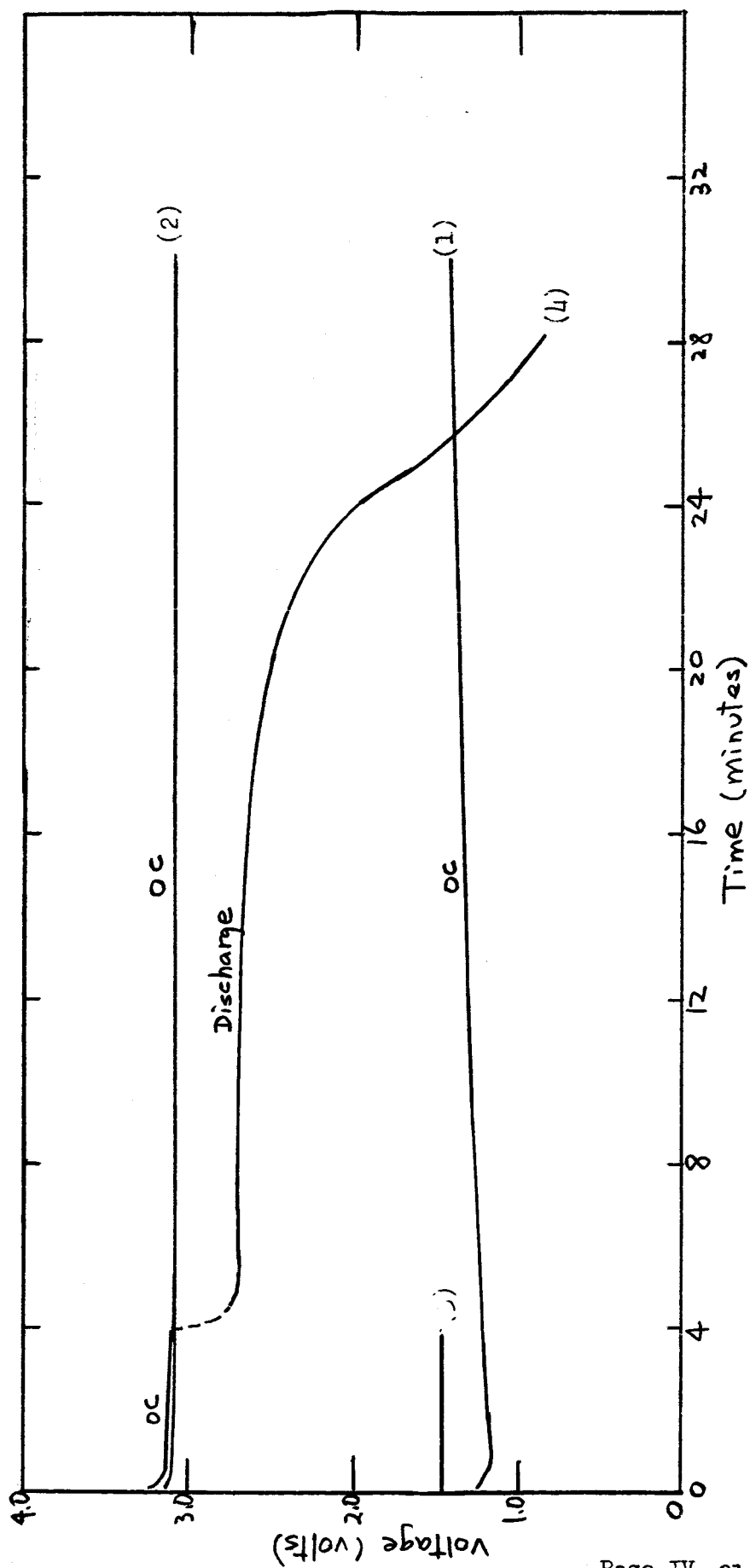
OCV after charge at 1 ma/cm² for 10 min.: 2.18 falls to 1.89 volts in 1 min.

OCV after charge at 1 ma/cm² for 70 min.: 2.22 falls to 1.80 volts in 3 min.

OCV after charge at 0.3 ma/cm² for 17 hr.: 2.42 falls to 1.91 volts in 3 min.

OCV after discharge at 10 μ a/cm² for 5 min.: 1.06 rises to 1.52 volts in 160 min.

Note: All current densities are approximate average values and are based on Mg anode area.



- (1) NiF₂-Ni cathode vs. Mg anode on O.C. before charge.
- (2) Cathode vs. anode on O.C. after 15 hours charge.
- (3) Cathode after charge vs. fresh Mg strip.
- (4) After charged at 11 ma/cm² for 30 minutes, cathode vs. anode on O.C. and on discharge (140-100 µa/cm²).

FIGURE 3. CELL POTENTIAL OF Mg/KPF₆-
PROPYLENE CARBONATE (0.96 molal)/NiF₂-Ni

FINANCIAL DATA

CONTRACT NO. NAS3-2790

Third Quarter - February to April 1964

	<u>Manhours</u>	<u>Amount</u>
Labor	1278	\$3,211.41
Burden (90%)		<u>3,790.27</u>
		\$7,001.68
Materials and Supplies		<u>2,088.44</u>
		\$9,089.12
General and Administrative 10%		<u>908.91</u>
		\$9,998.03

April 1964

Labor	302	\$ 919.92
Burden (90%)		<u>827.93</u>
		\$1,747.65
Materials and Supplies		<u>795.09</u>
		\$2,542.94
General and Administrative 10%		<u>254.29</u>
		\$2,797.23

Estimated commitments for supplies - none.